

Remarks

1.1. In the official action of 12 June 2007, the Examiner has maintained his rejection of claims 1-4, 6-8, 10-20 (all current claims) relying on the Golem and Dufresne references previously cited and discussed.

1.2. The amendments to claims 1, 18 and 20 are by way of emphasis, that the regeneration which takes place in the claimed process is not carried out in a regenerator which is integrated with the reactor train. This the concept underlying the invention as originally disclosed, where the objective is to avoid or, at least, defer the cost of the moving bed regenerator.

1.3. Applicant adheres to the arguments previously presented in the response of 2 August 2006 and refers to that response for a complete statement and analysis of the present invention and its relationship to the prior art in general and to the cited references in particular¹. In order for Applicants' arguments to be followed more easily, however, a summary of the invention and its relationship to the references is given below.

1.4. This present invention resides in a method or scheme for converting fixed bed catalytic reforming units to moving-bed reactor operation. The conversion, however, is not a full conversion in which, in the finished unit, the reforming catalyst moves continuously through the serial moving bed reactors and then to the continuous regenerator but rather, is a low-cost partial conversion in which the fixed bed reactors are removed and moving bed reactors installed but the conventional fully-integrated regenerator characteristic of a complete moving bed continuous regeneration unit is not used. Instead, continuous or intermittent catalyst feeding facilities are provided to allow continuous or intermittent addition of fresh or regenerated catalyst to the catalyst inlet of the moving-bed reactor and continuous or intermittent removal of spent catalyst from the catalyst outlet of the last moving-bed reactor in the train of reactors. The spent catalyst removed from the reactor is regenerated in a non-integrated regenerator which may be an offsite regenerator, a centrally located on-site regenerator which serves several

¹ There is an error in Section 2 of the response: in the next to last line of the section "lower" should read "higher".

reforming units or a regenerator shared with a second moving bed unit. The converted unit is operated at an effective reactor pressure to improve reformat quality and yield compared to the reformat product from the fixed-bed unit before the conversion. Typically, this reactor pressure will be lower than that of the fixed bed unit whose reactors have been replaced but higher than the pressure which would be used in a full conversion to a continuous catalytic regenerator reformer with its own dedicated reactor.

1.5. The Golem reference is a paper which describes the commercial success of the UOP CCR Platforming™ process and acknowledges that refining economics may not always favor complete unit conversions. Three options for obtaining some or all the benefits of CCR Platforming technology are proposed (page 6). These are:

Hybrid CCR Platforming process

Full CCR Platforming process

New, Second Generation CCR Platforming process

Of these options, two (the second and third) are the full conversions to CCR with moving bed reactors and fully-integrated moving bed regenerators. The only lower cost alternative to the complete CCR conversions is a conversion to the Hybrid CCR Platforming process which utilizes the existing fixed bed reactors and adds a final moving bed reactor with its own associated regenerator (Golem, page 6) although replacement of one of the original fixed-bed reactors by the moving bed reactor appears as an alternative (second paragraph, page 7). Thus, in the partial conversion described by Golem *fixed bed reactors are retained in the train*.

1.6. Dufresne discloses an offsite process (column 3, line 31; column 4, line 33) for the regeneration of a used hydrocarbon treatment catalyst. The spent catalyst which may be regenerated by this process may be "from a continuous and/or semi-regenerative type reforming process, i.e., a continuous type, semi-regenerative type or mixed type process." (column 4, lines 16-19) and in cases when the catalyst is from a continuous reforming process, the off-site regeneration is intended to deal with upset conditions (see column 2, lines 44-59) such as where there is an excess amount of coke deposited on the catalyst during the reforming reactions.

2.1 Applicants' submissions with respect to the patentability of the present claims will now be made, with reference where appropriate to the Examiner's remarks set out in the office action.

2.2.1. *The present claims are directed to a conversion method.*

The preambles to claims 1, 18 and 20, the only independent claims in the application are as follows:

1. A method for the conversion of a fixed-bed catalytic reformer unit to moving bed reactor operation without a dedicated continuous catalyst regenerator,....
18. A method for the conversion of a fixed-bed catalytic reformer unit to moving bed reactor operation without a dedicated continuous catalyst regenerator,...
20. A method for the conversion of a fixed-bed catalytic reformer unit to moving bed reactor operation,...

In each case, the method is defined by the acts which take place during the method as well as by reference to the manner of operation of the unit following the conversion. In the conversion itself, *each* fixed bed reforming reactor of the original fixed-bed unit is converted to a moving bed reactor (claims 1, 18, 20) also, catalyst feeding facilities are added at the catalyst inlet of the reactor train and spent catalyst recovery facilities at the end of the train (claims 1, 18, 20). No integrated regenerator is provided (claims 1, 18, 20) and regeneration is carried out in a separate regenerator which may be a shared regenerator in another unit (claim 20). The mode of unit operation after the conversion is defined as one in which the spent catalyst is transferred to a non-integrated regeneration facility (claims 1, 18, 20) while the unit is operated at a lower pressure than it was before the conversion, referring to the pressure of the fixed bed reactors (claims 1, 18, 20).

2.2.2. *The conversion method is not suggested by Golem and Dufresne*

The Examiner acknowledges that Golem does not disclose a non-integrated catalyst regeneration facility but takes the view that it would have been obvious to modify the

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teachings of Golem by using an offsite regenerator as suggested by Dufresne on the basis that the use of an offsite regenerator as suggested by Dufresne would allow better control of the two principal regeneration steps (action, page 4).

It is not contested that Dufresne discloses offsite regeneration with its attendant advantages quite explicitly but even if, *ex hypothesi*, the Dufresne disclosure be read in the light of Golem to suggest the desirability of using offsite regeneration with a unit of the type described by Golem, there would still be no teaching of the presently claimed conversion method. Golem does not disclose or suggest the present conversion method in which *each* fixed bed reforming reactor of the original fixed-bed unit is converted to a moving bed reactor to form a unit with no integrated regenerator. In the Golem Hybrid conversion, the moving bed reactors are retained and so a key feature of the present claims, namely, that *each* fixed bed reactor is replaced by a moving bed reactor is not met. In addition, a regenerator for the moving bed reactor is installed (Golem, page 7). In the full CCR Platforming conventions (second and third Golem options), all the former fixed bed reactors are replaced, admittedly, but in these cases, a fully integrated, dedicated regenerator is installed. Claims 1, 18 and 20 preclude the presence of the dedicated regenerator which is part of each of the two full conversion schemes described by Golem. Claim 20 requires the use of a shared regenerator which is integrated with another reactor train (as described, for example, in Section 0012) and Golem does not suggest such a manner of operation at all. Thus, the revamps described by Golem are different to the presently claimed scheme and even if Dufresne be read in the light of Golem to suggest the desirability of off-site regeneration after one of Golem's conversions, the claimed overall conversion and operational scheme is not rendered obvious.

The Examiner has asserted that "The revamp in the manner disclosed by Golem is believed to result in a unit that is operated as claimed" (office action, page 4, top). For purposes of analysis, it might have assisted consideration if the Examiner had made clear which of the Golem revamp options was in mind here since, as pointed out above, there are three revamp options described. In any event, however, none of the Golem options makes the same conversion steps "to result in a unit that is operated as claimed". The Golem Hybrid option retains fixed bed reactors rather than converting each of them and the full conversion options offered by Golem – which the present

invention is directed to avoiding – utilize a dedicated, integrated regenerator which is not in accordance with the claimed conversion scheme.

As far as the Examiner's point about the pressure of the operation is concerned (office action, page 4), Golem concededly contemplates operation of the retained moving bed reactors with a "moderate pressure reduction" (page 6, bottom) in the Hybrid case and in the full conversions, a significant pressure reduction will also occur. The Hybrid case, however, is not the same conversion scheme now claimed. As pointed out above, the present invention provides a *different* scheme which is, in fact, intended to achieve most of the advantages of moving bed operation at lower cost and it does this by going to an operation which is entirely based on moving bed reactors, unlike Golem's Hybrid scheme which still retains fixed bed reactors rather than eliminating them. Golem's full conversions are also different in that a dedicated, integrated regenerator is installed, contrary to the concept underlying the present invention which is to avoid the high cost of the regenerator. Again, Golem's disclosure does not support the rejection as made.

The Examiner's supposed counter (office action, page 8) that because Golem discloses "[R]eplacement of the existing side-by-side reactor train with a modern, moving bed stacked reactor system" (citing Golem page 13, paragraph 1), Applicants' position set out above is incorrect, is a canard. The replacement referred to here by Golem is the *full* conversion in which all fixed bed reactors are replaced by moving bed reactors (as in the present invention) but Golem goes on also to install an integrated regenerator with its incident high cost as recognized by Golem: "*The cost of a larger regenerator is significant and the project cost approaches that of a full CCR Platforming conversion.*" (Golem, page 7, foot). The fact is Golem does not disclose or suggest replacement of a complete fixed bed reactor train by a moving bed reactor train without its associate integrated regenerator.

Incidentally, the Examiner's suggestion that "The actual pressures used would be based on the desired composition of the product and one having ordinary skill in the art would adjust such pressures accordingly" (action, page 4) is a rather too simple description of the manner in which the operating pressure for a reformer is set. The composition of the product is certainly one of the factors in the selection of appropriate operating conditions since low hydrogen partial pressure will favor the desired production of aromatics but, at

the same time, low hydrogen pressure will increase coke production and so, reaction conditions including pressure must be a compromise between high conversion to aromatics coupled with an acceptable rate of catalyst deactivation. See, for example, *Modern Petroleum Technology*, 4th Edition, Hobson et al (ed.), Applied Science Publishers Ltd., 1973, ISBN 085334 487 6, pp. 330, 337, attached. So, the skilled person would select the pressure to be used in the process in accordance with established principles in which the composition of the product would be but one factor.

2.3.2. *Golem's "phased approach" is not a disclosure of non-integrated regeneration*

On pages 5-6 of the action, the Examiner has argued that Applicants' position that Golem's three conversion options do not result in a scheme of the type claimed is "not persuasive". In support of his position, the Examiner states that Golem discloses the following:

"If the revamp is the first step in a phased approach toward full CCR (continuous catalyst regeneration) platforming operations, the CCR regenerator is sized for use with the last moving bed reactor and a future reactor stack, which replaces the side-by-side reactors, or with a future reactor stack that replaces the entire reactor train".

From this, the Examiner continues by pointing out that Figures 9-11 of Golem "clearly show regenerator units separate from the reactor train" and from this concludes that "[T]his regenerator can be operated as a non-integrated regeneration facility or as a shared regenerator".

With respect, neither the quotation nor the Figures, nor the reasoning based on them, support a conclusion of obviousness. First, when a phased approach revamp is carried out, according to Golem, an oversized CCR regenerator is installed, to be big enough for the last moving bed reactor and a future moving bed reactor stack. The Examiner is correct in stating that such a regenerator "can" (*sic*) be operated as a non-integrated regeneration facility or as a shared regenerator. But mere capability is not the test of obviousness under 35 USC 103. For the claimed invention to be obvious within the purview of 35 USC 103, the prior art in and of itself must speak to the desirability of the claimed elements. *In re Gordon* 221 USPQ 1125, 1127 (Fed. Cir. 1984). So, the fact that the oversized regenerator of Golem's "phased approach" unit "can" be operated as

a non-integrated facility or as a shared regenerator does not posit a proper test of obviousness.

That Figures 9-11 of Golem show regenerators "separate from the reactor train" is hardly surprising. The regenerator is always constructed with some separation from the reactors both for reasons of design convenience and also for safety: the regenerator has its own requirements in terms of feeds and utilities (air, power) and it is obviously easier to design the regenerator around these factors, especially in the case of the "phased approach" when the regenerator is to have design criteria not fixed by the initial state of the reactors. Second, safety plays a significant part in the design considerations: the reactors work in a high temperature, hydrogen-rich atmosphere where as the regenerator operates in a high temperature, oxygenated atmosphere, a sure formula for disaster if the two atmospheres should become mixed. Thorough purging of the spent catalyst is required before it can enter the regenerator both to remove occluded hydrogen as well as hydrocarbons. The depiction of the regenerator as a separate component or sub-unit in Figures 9-11 of the Golem reference therefore provides no indication that the skilled person would interpret that disclosure as pointing towards the use of a moving bed reactor train without an integrated regenerator (claims 1, 18) or of a shared regenerator (claim 20).

2.3.3. *The disclosed advantages of Dufresne's off-site regeneration do not motivate the use of non-integrated regenerators for use with units having no integrated regenerator.*

Dufresne discloses the advantages of his off-site regeneration process with its two characteristic steps of oxidative coke removal followed by oxyhalogenation, each carried out under carefully controlled conditions. The process is described as one which is capable of delivering a regenerated catalyst of improved characteristics (noble metal dispersion, surface area). These advantages concededly provide an incentive to use the Dufresne process in its intended manner which, as previously pointed out is as an adjunct to the normal CCR continuous regeneration in units with a train of moving bed reactors. Dufresne's process enables the refiner to avoid costly low-capacity operation or a costly catalyst changeout with a CCR unit (col. 2, ll. 44-59). In the case of a semi-regenerative unit (col. 2, ll 60-65), the down time following an upset may be even longer.

The context in which the Dufresne regeneration conceptually would take place following a unit conversion as taught by Golem, therefore, is as follows:

Golem Hybrid Conversion: Not all fixed bed reactors replaced. Dufresne process used for fixed bed catalyst at normal regeneration intervals and for moving bed catalyst after upsets. No suggestion that the hybrid converted unit should be built without integrated regenerator for the moving bed reactor(s) – in fact, Golem is to the contrary in stating that “CCR technology *requires* a moving bed reactor and a new regenerator” (Golem, page 7, fourth paragraph, emphasis added).

Golem Full CCR Conversion: All fixed bed reactors are replaced. Dufresne process used for catalyst after upsets. No suggestion that the converted unit should be built without integrated regenerator – in fact, Golem is to the contrary in stating that “Conversion to the full CCR technology requires replacement of the existing reactor train with a modern moving bed reactor system. A new CCR regenerator is added....” (Golem, page 8, third paragraph).

In either case, the fact that Golem does not suggest a unit conversion of all the original fixed bed reactors with moving bed reactors but no integrated regenerator makes the assertion of obviousness untenable, what motivation Dufresne’s advantages might be.

The Examiner’s argument (office action, page 9, foot) that the Dufresne invention applies not only to occasional departures from conventional integrated regeneration in the event of a unit upset but also to normal operation is correct for semi-regenerative operation but since Golem does not suggest unit conversion without an integrated regenerator, the point is not relevant since no hypothetical combination of Golem and Dufresne can arrive at the presently claimed invention. Dufresne spoke only to regeneration with the types of unit that were known, that is, to semi-regenerative units (fixed bed) and to CCR units and to units of the hybrid type with both fixed and moving bed reactors in which each type of reactor had its own catalyst and associated regeneration requirements. Dufresne did not speak to use with units of unknown type such as those now claimed and which are not taught by Golem, namely, units with only moving bed reactors but no integrated regenerator.

2.3.4. *Golem and Dufresne do not disclose or suggest the use of a shared regenerator*

Claim 20 is directed to the shared regenerator option under the present invention. The Examiner takes the view (office action, page 10, foot) that Golem shows an arrangement in Figures 10 and 11 where the regenerator is supplying the catalyst to the reforming unit. This, of course, is the normal manner of operation for a CCR regenerator. Dufresne, in its teaching of offsite regeneration of catalyst from a CCR unit requires that the catalyst be taken from the last reactor and then to the offsite regenerator. The offsite regeneration facility disclosed by Dufresne, however, is one which includes a moving bed furnace, a rotolouvre furnace or a belt furnace (column 4, ll. 4-9). None of these types is a shared regenerator and there is no suggestion that a regenerator from another CCR type unit might be used and so, the Examiner's position is not factually supported by the reference disclosure.

In view of the amendment and remarks set out above, reconsideration and withdrawal of the rejection are requested.

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The oil industry is ever changing and persist there are continuing innovations and other reasons it has become "Modern Petroleum Technology". The present team of authors have the various topics been treated but in many cases the approach. A short Appendix on metric units part of the world oil industry made to use these units in a very considerably increased manner.

The changes in the data have in no way altered the presentation sound and comprehensive in the oil industry, in a form which the newer recruits to the industry sound understanding of those.

The Institute wishes to re-examine the thirty chapters, and to a new edition. The planning and responsibility of the Abstracts Committee. Special thanks to its Chairman, Dr G. D. I. Mr George Richardson and the effort they have given to the

thus reducing compression costs for high-pressure processes such as hydrocracking or ammonia production. Pure oxygen is however required, which necessitates an air liquefaction plant. The cost of oxygen depends strongly on the scale of production. Below 10 MM scfd H_2 production capacity this might outweigh the other advantages unless there is a liquid nitrogen requirement.

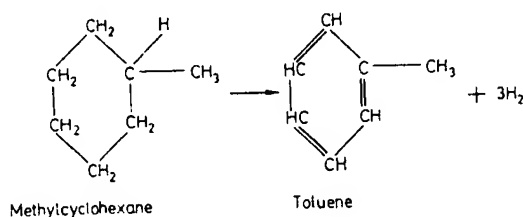
CATALYTIC REFORMING

Until about 1940 the octane number of straight-run naphtha was improved by thermal reforming, the improvement resulting mainly from the cracking of low-octane-number paraffins and the production of higher-octane-number olefins. Thermal processes are, however, somewhat indiscriminate in action and do not act very efficiently on a yield basis in transforming low-octane compounds to high-octane compounds.

Catalytic reforming, developed in the early 1940s, is a more efficient process for the production of high-octane-number hydrocarbons. The main constituents of catalytic reformer feeds are paraffins and naphthenes, which can undergo a number of reactions, the extent to which each reaction occurs depending on the catalyst and operating conditions.

The main reactions are:

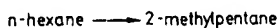
1. Dehydrogenation of naphthenes to give aromatics plus hydrogen



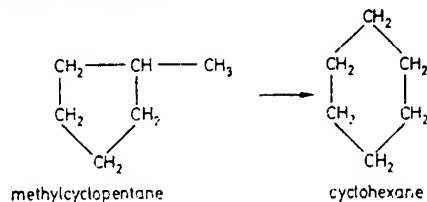
2. Isomerization

Paraffin isomerization is an effective reaction for increasing anti-knock quality for the lower molecular weight C_5 and C_6 paraffins only. The octane numbers of equilibrium mixtures of heavier paraffin isomers decrease rapidly as carbon number increases.

a) paraffin isomerization



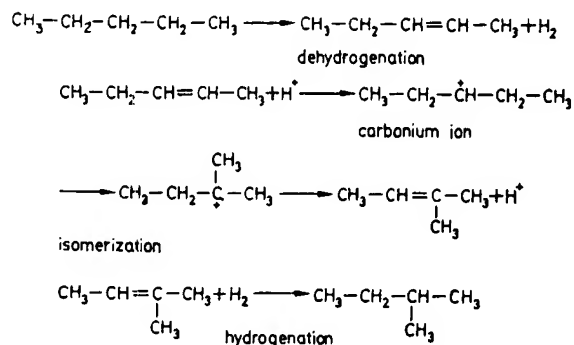
b) naphthene isomerization



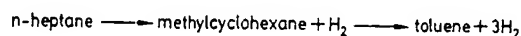
The olefins formed by the dehydrogenation of paraffins act as reaction intermediates, and are quickly removed by rehydrogenation, hydro-isomerization, and dehydrocyclization reactions, so that the final reformed naphtha contains only trace amounts of olefins.

The cyclohexane may be dehydrogenated to benzene by reaction 1.

Paraffin isomerization takes place by carbonium ion mechanism and involves both dehydrogenation and hydrogenation reactions:

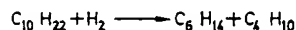


3. Dehydrocyclization



The cyclization also takes place by carbonium ion mechanism followed by dehydrogenation.

4. Hydrocracking



The initial step is the formation of a carbonium ion and subsequent splitting and hydrogenation.

In the first three reactions the number of carbon atoms in the molecule remains unchanged and the yield of the high-octane-number product is almost 100 per cent wt (loss of hydrogen in dehydrogenation, but no loss in isomerization). Hydrocracking, however, causes a molecular breakdown and thus a loss in gasoline yield as the cracking produces C_1 to C_4 fragments that are below the gasoline boiling range. The C_5 and higher products can undergo further reactions of isomerization or dehydrocyclization to give more high-octane-number material.

Except for the shifting of attached alkyl groups along the ring, the aromatics formed by these various reactions are stable at normal catalytic reforming conditions. At higher severities, substituted aromatics may dealkylate.

Small amounts of aromatic polymers containing naphthalene, anthracene, and heavier compounds are also formed. Reactions involving these compounds probably lead to the formation of coke on the catalyst surface.

Naphthene dehydrogenation to aromatics and paraffin dehydrocyclization are strongly endothermic (800–1000 Btu/lb) while hydrocracking is exothermic

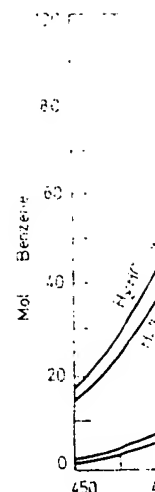


FIG 34. Equilibrium distri

(approx. 150 Btu/lb for the exothermic.

The largest gain in octane and paraffins into aromatics by isomerization is only of limited value. Isomerization is only of limited value for branched isomers (high octane number) relatively low at the temperature. Improving the octane number

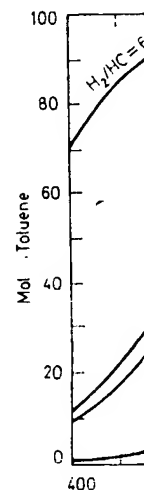


FIG 35. Equilibrium distr

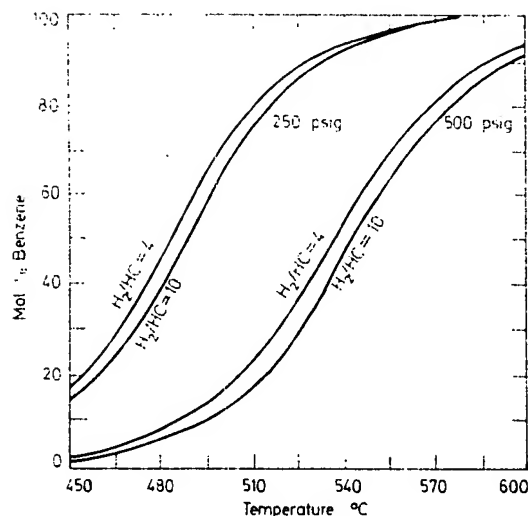


FIG 34. Equilibrium distribution for the system n-hexane/benzene/hydrogen.

(approx. 150 Btu/lb for the reaction 4 above) and isomerization is slightly exothermic.

The largest gain in octane number is obtained in the conversion of naphthenes and paraffins into aromatics by dehydrogenation and dehydrocyclization reactions. Isomerization is only of limited value as the equilibrium concentration of highly-branched isomers (high octane) falls rapidly with increasing temperature, and is relatively low at the temperature used in catalytic reforming. Hydrocracking improves the octane number of the product, partially by breaking up, and thus

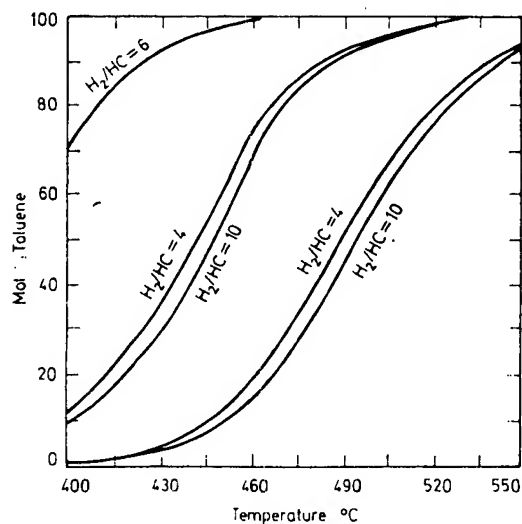


FIG 35. Equilibrium distribution for the system n-heptane/toluene/hydrogen.

Under these high-temperature, low hydrogen partial pressure conditions coke was deposited on the catalyst, which necessitated regeneration after 4-8 hours processing. Cyclic operation was therefore required using multiple reactors. A simplified flow diagram is given in Fig 36, which shows a four-reactor system, two processing and two regenerating. Fresh feed and recycle gas are preheated to reaction temperature in separate heaters and passed to the first reactor. The highly endothermic dehydrogenation reactions cause the temperature of the reactants to fall by about 40-50° C in passing through the reactor, and they are then reheated and passed to the second reactor for further conversion. The products are cooled to about 40° C and passed to a separator from which the gas (containing approx. 70-80 per cent H₂) is recycled. The excess gas and liquid product are separated by absorption/distillation to recover C₃, C₄, stable gasoline, and the hydrogen-rich excess gas stream.

After some 4-8 hr on-stream the catalyst becomes deactivated and must be regenerated. Feed is switched to the other pair of reactors, and after purging out the hydrocarbons the offline reactors are regenerated, using a flue gas/air mixture containing 1-3 per cent oxygen. Catalyst temperatures are limited to 570-600° C by control of the oxygen content, and both upflow and downflow burning are used to ensure complete regeneration. The switching of reactors is carried out automatically using a timer, and the relative periods of reaction, purging and regeneration, are set to give the optimum results for the severity of the conditions employed.

The MoO₃-alumina also acts as a desulphurization catalyst and about 90 per cent of the feed sulphur is removed, mainly on to the catalyst where it is burnt to SO₂ during regeneration.

Under the conditions employed the conversion into aromatics is very high, and Hydroforming was much used to produce toluene and xylenes for aviation gasoline and explosives during 1939-45.

Typical feed and product qualities and yield data are given in Table XXII.

TABLE XXII
Fixed-Bed Hydroforming
Typical yield and product quality data

	Feed	Product
Sp gr, 15/15° C	0.78	0.78
ASTM distillation, °C		
IBP	79	40
10% vol	113	69
50% vol	154	127
90% vol	195	170
FBP	228	204
ON, Research, unleaded	39.7	80.3
ON, Research, + 3 ml TEL/US gal	..	91.0
Bromine No.	2.2	3.2
Sulphur content, % wt	0.220	0.015
Yields, % wt		
C ₃ and lighter	10.7	..
C ₄	7.8	..
Gasoline	76.0	..
Polymer	3.9	..
Carbon	1.6	..

To obviate difficulties in short processing cycles at high conversion, moving-bed and fluid-catalyst processes were developed, but few units were built. The problems of operating moving-catalyst systems containing hydrogen at approx. 300 psig in the process side and oxygen in the regeneration side were considerably greater than in catalytic cracking. This development appears to have been abandoned after the complete destruction of a fluid Hydroformer at Whiting in an explosion only six months after commissioning.

In 1949 UOP announced the Platforming process based on a platinum-alumina catalyst that was not regenerable *in situ* and was designed to give long on-stream times before replacement. This discovery of the use of platinum resulted in a rush of platinum-based reforming processes announced over the following few years. The process was developed along two main lines, one, arriving at long on-stream times, and the other operating with alternating processing and regeneration periods using swing reactors in a similar manner to Hydroforming. Table XXIII lists the main processes.

TABLE XXIII
Catalytic Reforming Processes

Process	Developed by	Date process announced
Fixed-bed hydroforming	Standard Oil Development Co M. W. Kellogg Co and Standard Oil Co (Indiana)	1939
Platforming	Universal Oil Products Co	Mar. 1949
Catforming	Atlantic Refining Co	Feb. 1951
Houdriforming	Houdry Process Corp.	May 1951
Thermoform catalytic reforming	Socony-Vacuum Oil Co, Inc.	May 1951
Fluid hydroforming	Standard Oil Development Co and M. W. Kellogg Co	May 1951
Hyperforming	Union Oil Co of California	Feb. 1952
Sinclair-Baker	Baker & Co with Sinclair Refining Co	May 1953
Orthoforming	M. W. Kellogg Co	July 1953
Ultraforming	Standard Oil Co (Indiana)	Nov. 1953
Sovaforming	Socony-Vacuum Oil Co Inc.	Jan. 1954
Rexforming	Universal Oil Products Co	Mar. 1955
Iso-plus	Houdry Process Corp.	Mar. 1955
Powerforming	Esso Research and Engineering Co	Mar. 1956
Magnaforming	Engelhard Minerals and Chemicals Corp.	Feb. 1965
Rheniforming	Chevron Research Co	May 1969

The difference between the two approaches is that of coke formation. In the long on-stream type, conditions of high hydrogen partial pressure (high plant pressure and hydrogen recycle) are maintained to inhibit coke formation, whereas the other method operates at lower pressures and allows for coke formation by incorporating facilities for frequent catalyst regeneration. As mentioned previously, the conversion of naphthenes into aromatics is reduced at high pressure, and therefore to obtain the same octane number more hydrocracking must be carried out to compensate for the lower aromatic production at high pressure. A comparison between continuous and regenerative conditions is shown in Table XXIV where it can be seen that the increased hydrocracking results in a lower gasoline yield, lower hydrogen production and higher C₂-C₄ yield. The regenera-

tive type process, however, needs switching reactors and regenerat

Comparison of Continuous

Feed, Kuwait naphtha
Sip gr, 15/15° C
ASTM distillation, °C
IBP
10% vol
50% vol
90% vol
FBP
Naphthenes, % vol
Aromatics, % vol
Paraffins, % vol

Operation

Yields, % wt
Hydrogen
Methane
Ethane
Propane
Butanes
Gasoline
Gasoline, ON, Residue

Feedstocks

Catalytic reformer feeds are at a maximum of about 190° C. In the naphtha, but other by-product processed after treatment to a cracker naphtha that contains a stable feed. It is not usual to include capable of giving increased octane ratio at reaction temperatures of the hydrocracking reaction break and thus reduces the yield of gasoline.

The yield of gasoline of a given conditions depends on the hydrocarbons which readily give high aromatic highest gasoline yields. Paraffins difficult isomerization, dehydro more severe conditions and give stocks. The difference becomes

The end point of the feed is an increased coke deposition on the because there is an increase in the feed end point avoids a redisp end-point specification of 205

tive type process, however, needs spare reactors and complicated pipework for switching reactors and regenerating the catalyst.

TABLE XXIV

Comparison of Continuous and Regenerative Catalytic Reformers

Feed, Kuwait naphtha		
Sp gr, 15/15° C	0.763	
ASTM distillation, °C		
IBP	115	
10% vol	139	
50% vol	154	
90% vol	169	
FBP	179	
Naphthenes, % vol	19.4	
Aromatics, % vol	15.5	
Paraffins, % vol	65.1	
	500 psig continuous	200 psig regenerative
Operation		
Yields, % wt		
Hydrogen	1.0	1.9
Methane	2.2	1.1
Ethane	4.5	2.4
Propane	7.2	3.4
Butanes	5.8	3.5
Gasoline	79.3	87.7
Gasoline, ON, Research	95.0	95.0

Feedstocks

Catalytic reformer feeds are saturated (*i.e.* not olefinic) materials boiling up to a maximum of about 190° C. In the majority of cases the feed will be a straight-run naphtha, but other by-product low-octane naphthas (*e.g.* coker naphtha) may be processed after treatment to remove olefins and other contaminants. Hydrocracker naphtha that contains substantial quantities of naphthenes is also a suitable feed. It is not usual to include C₅ in the cat. reformer feed as the only reaction capable of giving increased octane number is isomerization, and the equilibrium ratio at reaction temperatures does not give any great improvement. In addition, the hydrocracking reaction breaks C₅ wholly into fuel gas (C₂ + C₃ or C₁ + C₄), and thus reduces the yield of gasoline on feed.

The yield of gasoline of a given octane number and at given operating conditions depends on the hydrocarbon type analysis of the feed, high naphthene stocks, which readily give high aromatic gasolines, are the easiest to reform and give the highest gasoline yields. Paraffinic stocks, however, which depend on the more difficult isomerization, dehydrocyclization and hydrocracking reactions, require more severe conditions and give lower gasoline yields than do the naphthenic stocks. The difference becomes more marked at high octane numbers (Fig 37).

The end point of the feed is usually limited to about 190° C, partially because of increased coke deposition on the catalyst as the end point increases and partially because there is an increase in end point during processing of some 15° C. Limiting the feed end point avoids a redistillation of the product to meet the normal gasoline end-point specification of 205° C maximum.

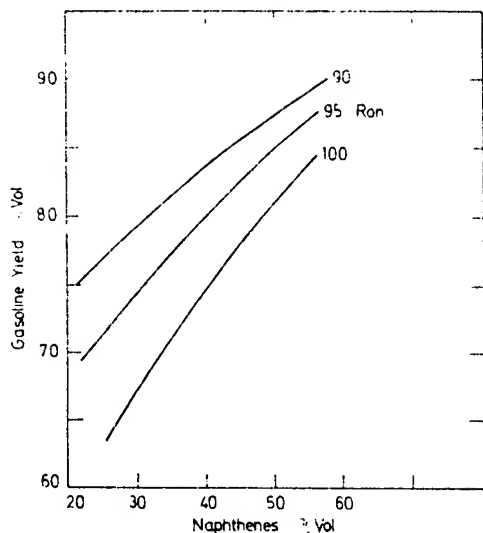


FIG 37. Gasoline yields.

Platinum is easily poisoned, and it is therefore necessary to exercise very careful control over contaminants in the feed to a catalytic reformer, the most important being as follows:

Sulphur

Under the high hydrogen partial pressure conditions used in catalytic reforming, sulphur compounds are readily converted into hydrogen sulphide, which, unless removed, will build up to a high concentration in the recycle gas. Hydrogen sulphide is a reversible poison for platinum, and causes a decrease in the catalyst dehydrogenation and dehydrocyclization activities. In the first catalytic reformers the hydrogen sulphide was removed from the gas recycle stream by absorption in, for example, diethanolamine. Modern units usually remove the sulphur from the feed by conventional desulphurization over cobalt-molybdenum catalyst. An additional benefit of desulphurization of the feed to a level of <5 ppm sulphur is the elimination of H_2S -corrosion problems in the heaters and reactors.

Nitrogen

Organic nitrogen compounds are converted into ammonia under reforming conditions, and this neutralizes acid sites on the catalyst and thus represses the activity for isomerization, hydrocracking and dehydrocyclization reactions. Very small quantities (1–2 ppm) can have an adverse effect. Normally, straight-run materials do not present serious problems with regard to nitrogen, but feeds such as coker naphtha may contain around 50 ppm nitrogen. Removal of this quantity may require high pressure hydrogenation (800–1000 psig) over nickel-cobalt-molybdenum on alumina catalyst, reported to be more efficient for nitrogen removal than cobalt-molybdenum.

Metals

Platinum is extremely sensitive and can have an effect at a level of a 10^9 . Arsenic is present probably as arsenic compounds used as an antiknock. Lead is the most common contamination with TEL or TML through the crude distillation and is easily removed if the reformer feed is desulphurized, which is less sensitive.

Water

Control of the water content is necessary to obtain the best results. A sudden increase in water content of the catalyst resulting in high gas molar ratio.

Chlorine

Organic chlorine in the feed can be a problem. This is discussed together with sulphur.

Catalyst

The purpose of platinum on a catalyst is to promote the cracking, and rapid hydrogenation to have an activity for isomerization, cracking step of hydrocracking, must have an acid activity. The catalyst must be important in a reforming catalyst. For example, it is important that hydrocracking is thus the acid activity should be from a paraffinic feed, where it is an important part.

The acid activity can be obtained by chlorine up to about 1 per cent on alumina base. Platinum content is 0.8 per cent wt. At higher levels and naphthene ring opening, catalysts tend to be less resistant.

The choice of platinum content of the catalyst represents a substantial reduction of capital invested between regenerations and a high-platinum catalysts (0.6–0.8 per cent).

Metals

Platinum is extremely sensitive to arsenic, lead and copper poisoning. Arsenic can have an effect at a level of a few parts/ 10^9 and lead and copper at 20–30 parts/ 10^9 . Arsenic is present probably because of contamination in the oilwell with arsenic compounds used as inhibitors during acid treatment of the well to increase production. Lead is the most common poison, entering the feed through contamination with TEL or TML in storage, or the processing of leaded slops through the crude distillation unit. These contaminants are normally removed easily if the reformer feed is desulphurized, and are deposited on the desulphurizer catalyst, which is less sensitive than the platinum catalyst.

Water

Control of the water content of the feed, and hence of the recycle gas, is necessary to obtain the best results, and is discussed later under water content. A sudden increase in water content will raise the hydrocracking activity of the catalyst resulting in high gas make and lower gasoline yield.

Chlorine

Organic chlorine in the feed can, like water, increase the hydrocracking activity. This is discussed together with the effect of water.

Catalyst

The purpose of platinum on the catalyst is to promote dehydrogenation and hydrogenation reactions, *i.e.* the production of aromatics, participation in hydrocracking, and rapid hydrogenation of carbon-forming precursors. For the catalyst to have an activity for isomerization of both paraffins and naphthenes, the initial cracking step of hydrocracking, and participate in paraffin dehydrocyclization, it must have an acid activity. The balance between these two activities is most important in a reforming catalyst and, in fact, may require to be different for different duties. For example, in the production of aromatics from naphthenes it is important that hydrocracking should be minimized to avoid loss of yield, and thus the acid activity should be lower than in the case of gasoline production from a paraffinic feed, where dehydrocyclization and hydrocracking play an important part.

The acid activity can be obtained by means of halogens (usually fluorine or chlorine up to about 1 per cent wt in catalyst) or silica incorporated in the alumina base. Platinum content of the catalyst is normally in the range 0.3–0.8 per cent wt. At higher levels there is some tendency to effect demethylation and naphthene ring opening, which is undesirable, while at lower levels the catalysts tend to be less resistant to poisons.

The choice of platinum content of the catalyst is, in general, one of economics. Platinum is extremely expensive (about £50/troy ounce) and the metal content of the catalyst represents a substantial amount of capital tied up. As the platinum content of catalyst is reduced its resistance to deactivation is also reduced, and the reduction of capital invested must be balanced against the reduction of time between regenerations and a reduction of ultimate catalyst life. Normally, the high-platinum catalysts (0.6–0.8 per cent wt Pt) are used for severe operations

such as the production of 100 octane number gasoline from feeds with only moderate naphthene contents.

According to patents, catalyst can be prepared by precipitating an alumina hydrogel by reaction of ammonium hydroxide with aluminium chloride and washing the gel until the chlorine content is less than 0.1 per cent wt. The gel is filtered and reslurried, and the correct quantity of halogen (as HCl or HF solution) added. The platinum is then added in the form of chloroplatinic acid solution treated with H_2S . After mixing, the gel is dried, pelleted and calcined at about 500° C.

Another patent claims the importance of the presence of a large proportion of alumina trihydrate in the catalyst base. The alumina is precipitated from aluminium chloride with ammonium hydroxide and the gel, after washing to remove chloride to less than 0.2 per cent wt, aged for several days at a pH of about 8. It is claimed that the resultant alumina base has a large proportion of its available surface area in pore sizes in the 100–1000 Ångström units instead of in the 10–50 Ångström units in normal aluminas, and that these high-pore aluminas give catalysts which show lower rates of activity decline under reforming conditions. Small catalyst particles give the best activity, and it is normally produced either as $\frac{1}{16}$ inch spheres or $\frac{1}{16}$ inch extrudates.

The latest development is the use of bimetallic catalysts which incorporate other metals (rhenium and tin have been claimed) in addition to platinum. It is claimed that this catalyst can operate at lower hydrogen partial pressures than can the normal platinum catalyst without deactivation. It is thus possible to take advantage of the increase in gasoline yield associated with lower pressure operation without incurring the penalty of short catalyst life. This development could also mean that in certain cases it may be possible to use catalysts of lower platinum content than previously, thus reducing the amount of capital tied up in platinum.

All catalysts are reported to be regenerable a number of times provided there has been no poisoning.

Process Variables

Temperature

Increasing the reaction temperature results in an increase in product octane number because of the increased rate of reaction. Normally, reactor temperatures are in the range 450–540° C; below 450° C the reactions are too slow and at around 540° C the rate of the hydrocracking reaction becomes excessive, with resultant loss of yield. Thermal cracking also occurs at around this temperature, leading to coke deposition on the catalyst. The thermodynamic equilibria are more favourable to aromatic formation at high temperatures, which also inhibit the reversible reaction of some naphthene isomers to paraffins, thus becoming more susceptible to hydrocracking.

Space velocity

The space velocity (vol feed per hour per vol catalyst) required to achieve a given severity will depend on the hydrocarbon types present in the feed. With high naphthene stocks a high space velocity can be used as the naphthene dehydrogenation reaction is very rapid. However, with more paraffinic stocks a lower space velocity will be necessary so that the desired conversion can be achieved

with the much slower hydrocracking. Increasing the temperature will of course increase severity. A combination of temperature limitations outlines velocities of 2–3 are normally used for selected high naphthene cuts.

Pressure

Increasing pressure increases aromatic equilibrium concentration. Pressure is increased.

Hydrogen/oil ratio

Hydrogen to oil ratio changes its effects are therefore similar to other processes, where carbon laydown about 3–5/1 but where long life between 5 and 10 : 1 are employed. Of course, an economic incentive to adequate life because of the high comparison of approximate compression ratios for various hydrogen/oil mole ratios.

Influence of

Hydrogen/oil mole ratio
Charge heater duty, 10⁶ Btu
Recycle compressor, bhp

Water content

Water entering the plant will be in equilibrium between the recycle gas and the feed. The amount of water passing over the feed and that in the recycle gas.

The immediate effect of an increase in the hydrocracking reaction is a loss of gasoline yield, and will be in the recycle gas, partly because of the reaction, and the amount produced because the hydrocracking reaction uses the hydrogen in the recycle. Catalyst life and hydrogen partial pressure and water is necessary however as high water content in the feed of less than 100 ppm will reduce catalyst life.

With catalysts containing chlorides of water tends to strip off chlorine. If too much water is reduced, the catalyst will be deactivated.

with the much slower hydrocracking and dehydrocyclization reactions. Increasing the temperature will of course increase the rate of all the reactions, and so the severity is a combination of temperature and space velocity effects, but with the temperature limitations outlined above. For motor gasoline production space velocities of 2-3 are normally used, but for aromatic production from specially selected high naphthene cuts space velocities up to 5 can be used.

Pressure

Increasing pressure increases the hydrocracking reaction but decreases the aromatic equilibrium concentration. Carbon deposition is also reduced as the pressure is increased.

Hydrogen/oil ratio

Hydrogen to oil ratio changes the hydrogen partial pressure in the reactor, and its effects are therefore similar to those of total pressure. In the regenerative processes, where carbon laydown is expected, hydrogen/oil mole ratio may be about 3-5/1 but where long life between regenerations is required ratios of between 5 and 10 : 1 are employed at a total pressure of 5-600 psig. There is, of course, an economic incentive to reduce the ratio to a minimum consistent with adequate life because of the high cost of circulating and heating the gas. A comparison of approximate compressor brake horse power and heat requirements at various hydrogen/oil mole ratios is given in Table XXV.

TABLE XXV
Influence of Gas Recycle Rate on Design

	Feed rate 10,000 bsd		
Hydrogen/oil mole ratio	6 : 1	8 : 1	10 : 1
Charge heater duty, 10 ⁶ Btu/hr	52.9	66.0	77.0
Recycle compressor, bhp	1,600	2,150	2,700

Water content

Water entering the plant with the feed will pass through the reactor, and will be in equilibrium between the recycle gas and liquid in the high pressure separator. The amount of water passing over the catalyst will therefore be the sum of that in the feed and that in the recycle gas.

The immediate effect of an increase in water content of the reactor feed is an increase in the hydrocracking activity of the catalyst. If excessive, this will lead to a loss of gasoline yield, and will also lead to a reduction of hydrogen concentration in the recycle gas, partly because hydrogen is consumed in the hydrocracking reaction, and the amount produced by dehydrogenation is reduced, and also because the hydrocracking reaction produces C₁-C₄ hydrocarbons which dilute the hydrogen in the recycle. Catalyst life also suffers because of the reduction in hydrogen partial pressure and increased production of coke precursors. Some water is necessary however as high demethylation activity has been reported with water content in the feed of less than 10 ppm.

With catalysts containing chlorine as the acid function promoter, the presence of water tends to strip off chlorine from the catalyst, and thus the long-term effect of too much water is reduction in hydrocracking activity as opposed to an